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AND
CEMENT MANUFACTURE

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Production of Cement and Iron in the Rotary Kiln.

By ADRIAN MARGARIT.

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A NEW process is being operated on a commercial scale at the Moncada Works, near Barcelona (the largest of the five mills owned by the Asland Company in Spain), for the simultaneous production of iron and Portland cement clinker in the rotary kiln. The patent used is that of M. Lucien Basset, a French chemist. Special conditions in Spain have contributed to the success achieved inasmuch as there are no blast-furnaces in the important industrial district of Catalonia, the cast-iron ingots required being obtained from the Cantabric coast (Vasconia, Santander, etc.).

The raw material from which the iron is obtained at the Moncada Works is burnt pyrites, a by-product in the production of sulphuric acid and superphosphates. Iron pyrites are very abundant in Spain. The burnt pyrites are submitted to further calcination which transforms them into ferric oxide, which is very suitable for use in the Basset process. The pyrites are mixed with coal and the calcareous and argillaceous raw materials used for the manufacture of Portland cement and introduced into a 9ft. by 140ft. dry process Allis-Chalmers rotary kiln to which few alterations have been made.

The material enters the kiln in the form of fine powder, which is slightly moistened so that it is not driven out by the powerful draught which the process demands. The action of heat dries and calcines the calcareous material, while the carbon monoxide reduces the ferric oxide and liberates the iron. As soon as the necessary temperature is reached, the clinkering process of the cementitious materials of the raw mix starts, the raw mix including the limestone and impurities with the ferric oxide and the coal. The molten iron remains at the bottom covered by a layer of solid slag or clinker, the composition of which is the same as that of good Portland cement clinker provided the raw mix has been properly made. The process avoids the reoxidation of iron by the action

of the oxygen in the air and by carbon dioxide and steam, which are also oxidising agents above certain temperatures. The atmosphere produced by the powdered coal burner and maintained by the coal mixed with the raw meal, which is free of dangerous quantities of carbon dioxide, ensures that the molten iron reaches the kiln exit without loss, the clinker only carrying with it about 1 or 2 per cent. of iron, a result which has not previously been obtained.

The clinker reaches the lower end of the kiln after flowing over a ring dam which retains the liquid iron. At this point the kiln shell has a discharge hole permanently open, and when this hole reaches the lowest position the iron flows through it and falls into a skip, which distributes it into either ingot tanks or into the mixing kiln. This skip is mounted on wheels running on rails, and it can be towed to the casting floors. The kiln is lined with clinker bricks, which the kiln itself maintains and renews with the aid of a system for cooling the kiln shell by water sprays at the zone of highest temperature.

The presence of a large quantity of free lime during the process leads to the production of a perfectly desulphurated iron casting of excellent quality with any desired carbon content ; generally it contains about 4 per cent. of carbon. Sulphur is practically undetectable, and phosphorus is negligible. The silicon and manganese contents are low except when, by the addition of manganese peroxide to the raw mix, manganese cast iron is obtained with 2 to 3 per cent. manganese ; this quality is suitable for the manufacture of steel in the Martin-Siemens' furnace. In order to obtain siliceous cast iron, the molten iron is poured into a small rotary kiln where it is thoroughly mixed with ferrosilicon ; this kiln is fed by a powdered coal flame, which in addition to the heat necessary to keep the mix molten, produces the necessary reducing atmosphere of carbon monoxide which prevents the combustion and loss of the silicon. Iron castings are thus obtained with 1, 2 or 3 per cent. silicon, as desired.

The Portland cement so produced is of excellent quality. Tests made in accordance with the present Spanish Standard Specification have given the following results on 1 : 3 cement-sand specimens cured under water.

Age.	Tension (kg. per sq. cm.)	Compression (kg. per sq. cm.).
24 hours	24.7	200
7 days	29.2	260
28 ,, ...	33.0	350

The kiln used formerly produced 150 tons of standard cement clinker in 24 hours ; the production now is about 50 tons of cast iron and about 80 tons of Portland cement clinker in the same period. The kiln has produced several thousand tons of iron which has been well received in the market.

The small amount of metallic iron that is always carried with the clinker is removed by a magnetic separator which enables it to be returned to the kiln and recovered later. The iron still included in the clinker after this operation passes with the clinker to the ball mill and remains in the cement, but its amount is about the same as the quantity of steel particles from the grinding media, and

therefore does not prevent the Portland cement from passing standard specifications. Although the economical production of iron and cement simultaneously depends on the conditions prevailing in different countries, it is claimed that the technical solution of the problem is perfect.

Analyses of the iron ingot obtained at Moncada are—Standard cast iron: C, 4.061 per cent.; Si, 0.187 per cent.; Mn, 0.102 per cent.; S, 0.007 per cent.; P, 0.059 per cent. Siliceous cast iron: C, 3.80 per cent.; Si, 2.70 per cent.; Mn, 0.43 per cent.; S, 0.007 per cent.; P, 0.09 per cent. Manganese cast iron: C, 4.82 per cent.; Si, 0.10 per cent.; Mn, 2.60 per cent.; S, 0.008 per cent.; P, 0.085 per cent.

The application of the Basset process to the rotary kiln requires minor alterations such as the adaptation of the burner for a reducing flame; change of the coal quality, which must be lower in volatile matter; a cleaning bar to keep the lower section of the kiln free from excessive coating; a flow hole or discharge tap; a ring dam to hold the liquid iron inside the kiln immediately behind the flow hole; external cooling of the kiln shell; a new type of lining; and a few other alterations. The installation of skips, moulds, casting floors, etc., as used in blast-furnaces is of course also needed. The capacity of a factory operating the process must be sufficient to enable it to reduce its output of Portland cement to 60 per cent. without losing any part of the cement market, inasmuch as the remaining 40 per cent. capacity will be used for the production of iron. Coal consumption is much higher than for the production of Portland cement clinker only, but the excess heat may be recovered. The skilled workers need special training, but these are in a minority.

Hardening of Magnesia Cement.—By L. Chassevent (*Verre et Silicates Ind.*, Vol. 6, pp. 25–26, 1935).—The setting of cement consisting of magnesia and magnesium chloride is due to the formation of $MgCl_2.3MgO.11H_2O$ which is in equilibrium with a 10 to 12 per cent. solution of $MgCl_2$ at room temperatures. From X-ray studies it has been found that $Mg(OH)_2$ does not separate during hardening and no change in oxychloride has been found after several months. The setting times (Vicat needle) for pastes made with magnesia burnt at 720 to 775 deg. C. for 24 hours and 106 g. MgO in 100 cc. of solution varied from 58 minutes for a 31.7 per cent. solution of $MgCl_2$ to 10.5 minutes for a 5 per cent. solution; with plain water the setting time was 140 minutes. For low concentrations of $MgCl_2$ the setting time was short but the strength low. Good strengths were obtained with concentrations of over 20 per cent. $MgCl_2$. By raising the $MgCl_2$ concentration from 20 per cent. to 30 per cent. the compressive strength rose from 250 to 1,250 kg. per sq. cm. For MgO burned at 750 deg. C. the 24-hour and 7-day strengths were practically the same. Raising the burning temperature reduces the strength and lengthens the setting time. This appears to be due to the increase in size of the MgO crystals and consequent reduction of surface area.

Cement Manufacture in New Zealand.

By M. W. von BERNEWITZ.

THERE are two cement plants in New Zealand, one in the North Island and one in the South Island.

At Portland, North Island, 121 miles north-east of Auckland by rail, Wilsons (N.Z.) Portland Cement, Ltd., makes ordinary Portland cement, rapid hardening Portland cement, and hydraulic lime or masonry cement in a plant which the writer visited in September 1933. The writer is indebted to Mr. F. W. Wilson, secretary, Mr. Stanley Reid, general manager in Auckland, Mr. T. H. Wilson, works manager, Mr. F. N. Rhodes, and Mr. E. Leese, chief chemist, for their collaboration in the preparation of the following notes.

Fig. 1.—Part of Cement Rock Quarry.

The village of Portland is situated on sloping ground overlooking the works and the harbour. The village and 2,000 acres of land are owned by the company. The employees number 120.

Raw Materials

Cement Rock.—Fig. 1 shows part of the quarry for cement rock. The top is 280 ft. above the floor. The quarry is one mile by rail to the plant, and there is an almost unlimited reserve of rock in this and the adjoining hills. Under an overburden up to 24 in. in depth is argillaceous limestone containing 72 per cent. calcium carbonate, 22 per cent. silica, and 6 per cent. alumina and iron oxide. Seams of calcite are fairly common. A Sauerman dragline scraper is used to remove the cover.

The rock, which is fairly soft, is drilled and blasted. An electrically-driven 6-in. churn-drill can normally penetrate 40 ft. in eight hours. Twenty-five pound sticks of gelatine are placed at the bottom of holes and similar plugs of gelignite

near the top. The primer is placed near the bottom. Shots are fired by an electric blaster and Cordeau-Bickford fuse. One blast of 26 holes, the deepest of which was 240 ft., charged with 25 tons of explosives, moved 250,000 tons of rock. The average quantity removed is 4 tons of rock per pound of explosive. A blast in preparation had 18 holes, the deepest being 124 ft., and was charged with 6½ tons of explosives.

Broken rock is loaded into 7-ton side-tipping trucks by a 3-yd. Bucyrus electric shovel. A Ruston & Hornsby 1½-yd. steam shovel is kept in reserve. The quarry makes a little water. As many as 34 men have been employed here, and 1,400 tons of rock have been sent to the works in a day. Small steam locomotives haul rakes of 8 trucks, a load of 50 tons, to the works.

Limestone.—At Hikurangi, 15 miles from Portland, the company has a limestone quarry. Fig. 2 shows the present face, and Fig. 3 shows part of the

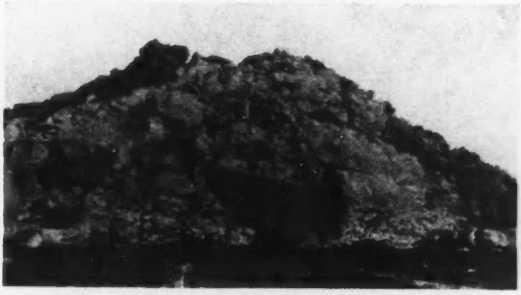

Fig. 2.—Face of Limestone Quarry.

remarkable outcrop. The lime rock has been considerably eroded and dissolved. Reserves are estimated as equal to thirty years' supply. The rock has 96 to 98 per cent. calcium carbonate content and a trace of silica and magnesia. Beneath the deposit is coal, which is mined for use at the works. As the rock is hard, drilling and blasting are necessary to break it into fairly large blocks, which are also drilled and blasted. A Diesel engine and compressor in the quarry produce air for the drills. Broken rock is loaded by hand on to flat trucks and dumped into wooden tubs on flat railway trucks; each railway truck holds three of these tubs containing two tons or more each. The daily capacity of the quarry is 200 tons.

Coal.—The coal mine is also at Hikurangi. The bed is 5 to 8 ft. thick and lies between a lower layer of clay and a layer of sandstone, above which is the limestone deposit. The coal is semi-bituminous and averages 6 per cent. each of moisture and ash, and 44 per cent. each of fixed carbon and volatile matter.

Ironstone.—Iron in the form of limonite, a bog iron ore, is added to the raw materials. This is obtained from small deposits between Hikurangi and Whangarei.

Gypsum.—The gypsum is imported from South Australia. It contains 94 per cent. calcium sulphate, the balance being silica, iron, alumina, and water.

Cement Works.

Fig. 4 shows part of the cement works, which has a daily capacity of 600 tons. The plant is designed for dry or wet manufacture, but the latter process is described here.

Handling Raw Materials.—The contents of the quarry trucks containing cement rock are dumped on to a screen and are reduced to 6-in. size in an Allis-Chalmers Fairmont roll crusher, and a bucket elevator lifts the crushed material to a screen with 3-in. openings. Oversize material is reduced in two gyratory crushers, and finally Fuller-Lehigh hammer mills or rolls, depending on the weather or tonnage, reduce the rock to 1-in. This is then fed into dryers or into wet tube-mills. If dry manufacture is desired, the dried rock is ground with limestone in seven 42-in. Fuller-Lehigh mills, whence it goes to the blending silos.

Fig. 3.—Eroded Limestone Outcrop.

The dryers measure 7 ft. by 60 ft., run at 3 revolutions per minute, and are fired with powdered coal. The limestone is crushed to 1-in. size in a No. 5 gyratory crusher and a hammer mill, after which it is conveyed by belt to the grinding mills. Coal is dumped by the Hunt system and taken by belt to a Fuller-Lehigh indirect-fired dryer; after drying, it is ground in 42-in. mills giving a product of which 95 per cent. passes through a 100-mesh sieve. Fine grinding of this class of coal gives better results than a coarser product.

Grinding.—Wet grinding is carried out by two Smidth tube-mills each measuring 7 ft. 3 in. by 36 ft., with three compartments, running at 19 revolutions per minute and using 600 h.p. each. Round table feeders deliver the 1-in. size cement rock, lime rock, and ironstone. The first two are in the proportions of 5 to 1, and about 3 per cent. of ironstone is added. The material is ground to a residue of 4 per cent. on a 180-mesh sieve. This material is elevated to concrete blending silos 16 ft. in diameter

by 60 ft. high with a capacity of 700 tons; the mix is agitated by compressed air. Thence it flows into a Smidth " sun-and-planet " slurry mixer, 120 ft. in diameter by 12 ft. deep. The main arm turns one revolution in four minutes, and the gear-driven stirrers suspended therefrom, alternately revolving in opposite directions, revolve four times a minute.

Calcining.—Two of the rotary kilns are 8 ft. 6 in. by 160 ft. throughout and two are 8 ft. in diameter by 160 ft. with a 9-ft. burning zone. They turn one revolution in two minutes, and are driven by a 35 h.p. variable-speed motor. Each has a capacity of 150 tons a day. They take either dry or wet mixture, and in the wet process are fed with a mix containing 42 per cent. of moisture.

The calcined product is cooled in four rotary coolers, drops into a shaking conveyor, passes over an Avery automatic weighing machine, and finally goes into storage bins. At a point about 33 ft. from the end of the kilns is a hole for the discharge of material that is prepared and sold as hydraulic lime or masonry cement.

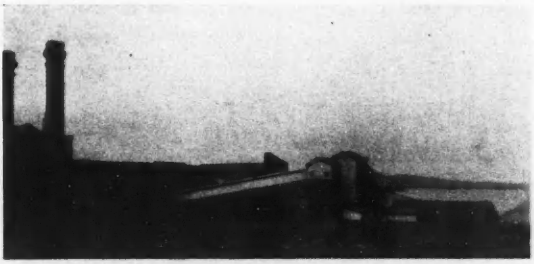

Fig. 4.—Part of Cement Works.

Clinker Grinding.—One Smidth mill similar to the wet mills and two 6-ft. by 26-ft. Allis-Chalmers mills with two compartments are used to grind the clinker with gypsum. Of the product, 3 per cent. remains on a 180-mesh sieve. These mills run at 19 revolutions per minute. The 3-compartment machine requires 600 h.p. and the 2-compartment machines 450 h.p. each.

Finished Cement.—From the grinding mills the finished cement is taken to 15 storage bins with a total capacity of 12,000 tons. Four Bates' machines are used to fill the jute sacks, containing 124 lb. each. As ship workers will not handle empty bags, none is returned, and the company is considering the use of paper bags. From the pack-house, cement is shipped by rail or by sea, mostly the latter.

Power.—At Wairua Falls, 17 miles from Portland, the company has a 2,000-kW. hydro-electric plant, which also supplies electricity to the town of Whangarei. Water power is supplemented by two Babcock and Wilcox waste-heat boilers, each with 12,000 sq. ft. of heating surface and supplied with heat from the kilns; these boilers can supply enough power for the whole works if necessary, and drive two British Thomson-Houston turbo-generators of 1,600 kW. each.

The Corrosion of Portland Cement in Water.

By E. B. R. PRIDEAUX and B. G. LIMMER.

FOR permission to publish the following we are indebted to the authors and to the *Journal of the Society of Chemical Industry*, in which journal the paper originally appeared.

The constituents of set, or hydrated, Portland cement are decomposed by exposure for a sufficient time to an excess of water. The dissolved material, about 30 per cent. to 40 per cent. of the original cement, consists mainly of lime, with small amounts of alumina, silica, and ferric oxide (which is soon precipitated); the residue becomes poorer in lime and eventually consists of hydrated silica and alumina (Lerch and Bogue, *J. Physical Chem.*, 1927, **31**, 1627).

Composition of Set Cement.

The hydration of ground cement clinker as described in the textbooks (e.g. Lea and Desch, *The Chemistry of Cement and Concrete*, Chap. IX, Arnold, 1935; Blount, *Cement*, Longmans, 1920) produces a mixture of fine lime, coarse lime in crystals, hydrogels, and hydrocrystalline silicates and aluminates of lime, of which the gels are at least as important as the crystals from the points of view of strength and hydrolysis. Lime which was originally "free" in the clinker slakes with expansion and probably yields mainly "fine lime" with the higher solubility, while lime originally combined with silica and alumina in the clinker becomes "free" on hydration and appears largely as a network of crystals, hexagonal plates, or short prisms. This "coarse" lime has the normal (lower) solubility, conductivity, and *p*H value.

Although the hydrated compounds mentioned later can exist permanently in contact with some solutions of high concentration in lime, yet when brought in contact with water they form incongruently saturated solutions which have compositions different from those of the solids. If it were not that these hydrated compounds and the products of their hydrolysis have rather low solubilities the attack of solid cement would be extensive. Water must be regarded as the primary agent of corrosion, since it is usually present in enormously greater proportion than any dissolved acid or salt. Substances dissolved in natural waters chiefly affect permeability of the outer corroded layers which protect cement from further attack. From this point of view waters may be classed as (*a*) acid waters containing hydrogen sulphide and humic acid which give soluble salts with lime; (*b*) pure waters; (*c*) waters containing bicarbonates and free carbonic acid; (*d*) saline waters.

In the present paper we have investigated the effect of pure waters, which depends only on hydrolysis and diffusion, and can be followed by physical methods. In addition we have investigated differences between the action of pure and ordinary hard water. The effects of carbonic acid and bicarbonates in larger amounts will, it is hoped, be described in a later communication.

The Separate Constituents.

Some of the principal constituents which have been recognised in cement clinkers with their common abbreviations, are as follows: $3CaO,SiO_2$ (C_3S); β-$2CaO,SiO_2$ (β-C_2S); α-$2CaOSiO_2$ (α-C_2S); $3CaO,Al_2O_3$ (C_3A); $5CaO,3Al_2O_3$ (C_5A_3); $2CaO,Fe_2O_3$ (C_2F); $4CaO,Al_2O_3,Fe_2O_3$ (C_4AF). These compounds have been prepared separately and their reactions with water have been examined (Lerch and Bogue, loc. cit.; Shepherd, Rankin, and Wright, *Z. anorg. Chem.*, 1911, **71**, 19; Lea, *Chem. and Ind.* 1935, 522; Rankin, *J. Ind. Eng. Chem.*, 1911, **3**, 211).

C_3S hydrates and hydrolyses with liberation of crystalline and fine lime. This easily forms solutions containing up to 1.29 g. of CaO per litre, instead of 1.16 g. per litre which is the concentration of the saturated solution of crystalline lime. The supersaturated solution soon deposits lime as crystals, or the lime combines with alumina. The product of hydrolysis of C_3S is sound and strong, and shows no anhydrous grains after three hours; hence it is supposed that C_2S is hardly formed as an intermediate product but that a hydrated metasilicate is produced at first: $3CaO,SiO_2 + 4H_2O = CaO,SiO_2,2H_2O + 2Ca(OH)_2$ C_2S hydrates and hydrolyses more slowly, about 0.1 per cent. in one day, and much unhydrated material is found after two years (Lerch and Bogue, *Ind. Eng. Chem.*, 1934, **26**, 837). Monocalcium or metasilicates give a much lower alkalinity, corresponding to CaO = 0.052 g. per litre. Hydrated C_2S and C_3S are also said to interact with liberation of lime and production of CaO,SiO_2,xH_2O. Hydrolysis of silicates appears to be almost irreversible at any rate down to the *CS* stage. It has been shown (Building Research Stat. Ann. Rept., 1933) that combination occurs between lime-water and gelatinous silica with the production of an amorphous product having nearly the composition *CS*, but that this is again hydrolysed by pure water with formation of a less basic silicate, such as C_2S or silica gel. Direct formation of C_2S can only take place slowly with the highest possible concentrations of lime-water.

Aluminates.—A great variety of these, including crystalline compounds, has been described. In small amounts of water C_3A hydrates, giving C_3A,xH_2O (x = 6 to 21) as hexagonal crystals which soon pass into the less soluble $C_3A,6H_2O$ crystallising in the isometric system (Travers, *Chim. et. Ind.*, 1932, **27**, 755; Lea, *J.S.C.I.*, 1935, **54**, 64 T). C_5A_3 hardens rapidly, and may form needles or plates with 30 per cent. of water, but also disintegrates in small amounts of water giving soluble alumina and amorphous, then crystalline C_3A,xH_2O (Rankin, *Trans. Faraday Soc.*, 1919, **14**, 33). C_3A may also be formed by recombination of the lime which is set free by hydrolysis of silicates, etc.: $5CaO,Al_2O_3,xH_2O + 4Ca(OH)_2 \rightleftharpoons 3[3CaO,Al_2O_3,yH_2O]$. CA and C_3A_5 hydrate in a similar manner yielding more amorphous alumina, thus: $2[CaO,Al_2O_3,aq.] + aq. \rightarrow 2CaO,Al_2O_3,7H_2O + Al_2O_3,aq.$

The most basic aluminates, $C_3A,12H_2O$ and C_4A, $12H_2O$, are in equilibrium with CaO = 1.08 g. per litre or more, whilst $C_3A,7H_2O$ is in equilibrium with CaO = 0.16 g. per litre. The reverse reaction, between lime-water and alumina,

has been confirmed by Travers (loc. cit.), who finds that $Ca(AlO_2)_2$ is first produced at *p*H 11.57 whilst at *p*H 11.62 $C_3A,21H_2O$ is precipitated. The *p*H of hydrolysed aluminates is also given as 11.6 to 11.7 by Kuhl and Berchem (*Zement*, 1932, **21**, 547). Titration curves of aluminium salts with lime have been published by Britton (*J.C.S.*, 1925, **127**, 21; 1927, 422), who finds that alumina dissolves from *p*H 8.5 to 10.5, at a molar ratio of about $CaO : Al_2O_3 = 1 : 1$, whilst a fine precipitate containing calcium and aluminium appears at *p*H 11.7.

From all these results, it seems clear that in setting and subsequent hydrolysis, aluminates act largely as complementary to silicates, taking up lime in several ways, and by a buffer action, keeping down *p*H so that the silicate hydrolysis can proceed.

Ferrites.—Ferrites appear to be hydrolysed irreversibly. C_2F stiffens on hydration without developing strength, whilst ferro-aluminates C_4AF develop strength especially in presence of gypsum, absorb much water, and give crystalline C_3A,xH_2O with amorphous hydrated CF (Lerch and Bogue, loc. cit., 1934).

Sulphaluminates.—Sulphaluminates formed by the interaction of aluminates with gypsum are said to be the cause of the delay in setting which is induced by the presence of gypsum: $3CaO,Al_2O_3 + 3CaSO_4 + 32H_2O \rightarrow 3CaO,Al2O_3, 3CaSO_4,32H_2O$. The presence of this "high sulphate" compound tends to reduce *p*H. There is also a "low sulphate" compound $3CaO,Al_2O_3, CaSO_4,12H_2O$ which is stable in solutions of high *p*H (Lerch, Ashton, and Bogue, *Bur. Stand. J. Res.*, 1929, 2, 715).

Further Hydrolysis and the Extraction of Soluble Constituents.

Information as to the further hydrolysis of the separate compounds is chiefly derived from the papers by Lerch and Bogue (loc. cit.), whose experiments followed three main lines.

(1) Extraction with 200 c.c. of water of such a weight of the compounds as would yield enough lime on complete hydrolysis to saturate the water. *p*H was determined electrometrically at the beginning and after attainment of equilibrium. Results are given in a table, which is reproduced below in an abstracted form.

Solid	$Ca(OH)_2$	C_3S	β-C_2S	α-C_2S	C_3A	C_5A_3	C_2F
Initial *p*H	12.1	11.56	11.08	10.01	11.70	11.43	10.25
Final *p*H	12.28	12.01	11.47	11.27	11.92	11.46	11.12
After hours	3	192	288	288	24	24	192

None of the compounds gives up all its lime, but an equilibrium is established with a less basic silicate or aluminate.

(2) Solutions of lime were added to check or reverse hydrolysis. C_3S increased the *p*H even of a solution saturated with $Ca(OH)_2$, giving one containing 1.286 g. of CaO per litre. The other compounds reduced the *p*H of lime solution to various extents, indicating some recombination.

(3) Molar equivalents of the compounds were extracted successively with larger quantities of water, e.g. 900 c.c. to 5 g. of C_3S. C_3S hydrolysed rapidly at first, more than 33 per cent. of the lime being removed in four days, and about 98 per cent. in 112 days; α-C_2S lost 7.8 per cent. in four days, 96 per cent. in 112 days; β-C_2S lost 8.8 per cent. in four days, 98.5 per cent. in 112 days. Several months were required to remove all the lime from aluminates and ferrites by percolation on a Soxhlet extraction thimble. (See also Colony, *Cement*, 1932, **5**, 285; Werner, *Tekn. Tidsk.*, 1930, **60**, No. 37, Kemi, 57, 68.)

Choice of Material.

Several kinds of cement which have been used commercially, e.g., for making centrifugally-spun concrete pipes, were kindly supplied by Mr. Woodhouse, Chief Chemist of the Stanton Ironworks Co., Ltd. The sample of Portland cement used in the present work contains the customary small percentage of gypsum retarder. It was shown by Koyanagi (*J. Soc. Chem. Ind. Japan*, 1934, **37**, 243 B) that calcium sulphate diminishes the first solubility of lime, which may be high, up to 1.35 g. CaO per litre, and falls rapidly in the presence of saturated calcium sulphate; thus in three hours it reaches the equilibrium value characteristic of coarse or crystalline lime. We have proved that the sulphate is nearly all present in the first extract.

On the whole, initial conductivity is reduced due to lime, but on the other hand, it is increased by that due to calcium sulphate itself. The conductivity of the saturated salt at 25 deg. is 2.24×10^{-3}, and is about one fourth of that of saturated lime at the same temperature. The concentration of calcium sulphate is very far from saturation. The two errors tend to cancel out and do not seriously affect the use of conductivity as a measure of concentration.

Analysis of Cement.

The sample used was analysed several times by the method of Blount (Lectures on Cement, *Inst. Chem.*, 1912). The proportions of the principal constituents were in good agreement, had normal values, and in particular conformed with the standard specification for the lime-silica-alumina ratio = 2.58. In considering the distribution of basic and acidic oxides, it must be noted that a part of the lime was "free." According to Bessey (*J.S.C.I.*, 1933, **52**, 219 T), ground cement clinker contains variable quantities, from 0.4 to 5.2 per cent. of free lime, present chiefly as $Ca(OH)_2$, which has been produced by hydration of CaO at the expense of the gypsum. These percentage amounts were obtained by comparing the loss of water at 350 deg. ($CaSO_4,2H_2O$, hydrated silicates, etc.), with that at 550 deg. [these constituents together with $Ca(OH)_2$]. We have determined "free lime," both in the dry cement and in that which had set for 24 hours, by the method of extraction with a concentrated solution of sucrose (Meade, *J. Ind. Eng. Chem.*, 1918, **10**, 214). The dry cement (i.e. after treatment with sucrose only) contained about 3.3 per cent. of CaO, the set cement 11.7 per cent. (calculated on the dry material).

MEAN RESULTS OF ANALYSIS.

	g. %	Mols. per 100 g.
Insoluble in acid	0.31	—
Combined silica	22.0	0.367
Total lime	62.0	1.105
Alumina	6.73	0.066
Ferric oxide	3.5	0.021
Magnesia	1.13	0.028
Sulphur dioxide	0.91	0.0114
Loss on ignition	1.54	—
Alkalis, etc., by difference	1.84	—
Lime " free " and as $CaSO_4$	3.0	0.065

According to the information thus summarised, the set cement contains C_2S (CaO = 0.367 × 2 mols.), C_3A (CaO = 0.198 mol.), C_2F (CaO = 0.042 mol.); total, 0.974 mol. of CaO combined with acidic oxides. By subtracting from the acidic oxides the equivalent of the MgO (as metasilicate or meta-aluminate), the remainder, 0.946 mol. of CaO, is combined, and subtracting this from 1.105 gives 0.159 mol. as " free " and sulphate lime, whereas 0.065 was found by analysis. This is as close an agreement as can be expected in view of the uncertainty as to the role played by magnesium oxide and as to the behaviour of C_2F on setting also to the presence of aluminoferrites and sulphaluminates.

Thus the lime, although slightly below the average of modern cements, is sufficient for the hydrolysis, etc., mentioned, and agrees moderately well with the 0.21 mol. which, by analysis, was free in set cement and is produced chiefly by immediate hydrolysis of C_3S. This represents the lime reserve of set cement which can be counted on to give pH and conductivity approaching those of calcium hydroxide in one of its forms.

Standardisation by Pure Lime.

Some outstanding uncertainties in the solubilities of calcium hydroxide have been examined and largely resolved by Bassett (*J.C.S.*, 1934, 1270). Discrepancies between earlier results are largely due to the different solubilities of " coarse lime " which forms well-defined needle-shaped crystals and " fine lime." The latter variety attains equilibrium with water very quickly but the particle size increases very slowly, so that the usual tests of equilibrium between solid and solution largely fail. From Bassett's table it appears that at 25 deg, the solubility of coarse lime as CaO is 1.13 and of fine lime 1.29 g. per litre, as $Ca(OH)_2$ 1.50 and 1.70 g. per litre. Some lime prepared according to the method recommended by Bassett was shaken at 25 deg. with conductivity water prepared in a Hartley still, with tinned copper condenser. The conductivity was 9.63×10^{-3} mho, which assuming that $\kappa(Ca^{\cdot\cdot}) = 60$ and $\kappa(OH') = 196$ (therefore the limiting conductivity $\lambda_0 = 256$) corresponds to 1.395 g. of Ca(OH)2 per litre, or assuming the correctness of the figure 1.50, the degree of dissociation of saturated lime is 0.93. The saturated solution was diluted in definite ratios, the conductivities of these giving the experimental κ/C line of *Fig.* 1 (marked as ½ S.L. etc.). The

hydroxyl-ion concentration of the saturated solution was also determined by the hydrogen electrode against the half-cells: (1) hydrogen-platinum in standard

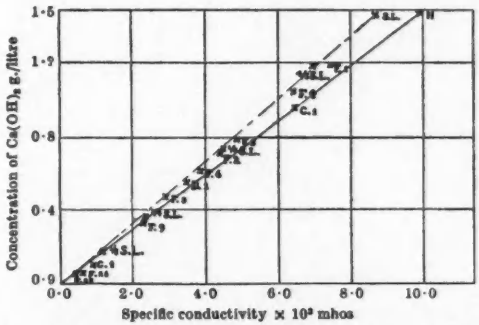

Fig. 1.—Conductivities and concentrations of lime derived from pure lime and cement.

acetate, (2) *N*-potassium chloride-calomel-mercury. The values obtained as pH were: 12.10, 12.25, 12.25, 12.2; mean 12.25. An electrometric titration of the saturated solution gives the solubility as 1.54 g. per litre. These are the limiting values of κ and pH towards which all extracts should tend.

Methods of Investigation.

Electrolytic conductivity proved to be most suitable for following the small changes of concentration of cement extracts. A temperature of 25 deg. was maintained throughout. The Kohlrausch method, using cells of low resistance capacity, was used for general routine work, but was checked on several occasions by a method which involves the measurement of fall of potential with a direct current, in a cell of high resistance capacity. The Kohlrausch and potential drop results are referred to as (*a*) and (*b*) respectively:

	(*a*)	(*b*)
Dilute lime solution	1.17×10^{-4}	1.20×10^{-4} mho
Cement extracts	1.24 ,,	1.26 ,, ,,
Hard water	3.65 ,,	3.85 ,, ,,
Saturated $CaCO_3$ in equilibrium with atm. CO_2	1.31 ,,	1.28 ,, ,,

Concentrations of lime were also determined by potentiometric and indicator titrations and usually agreed well with the conductivity results, showing that in these cases lime was the only important electrolyte present. In some cases, however, the titration results were distinctly higher, indicating the presence of soluble aluminates which would behave as free lime in titrations.

Results have on the whole been left as specific conductivities, which can be converted into concentrations of lime as required by the factor $Ca(OH)_2$ g. per litre $= 1.47 \times 10^2 \times \kappa$. The plain line in *Fig.* 1 has been calculated with the

aid of this factor from $74.1 \times 10^3/2 \times 256$. The broken line is experimental, having been obtained by diluting a saturated solution of lime with pure water.

Concentration $Ca(OH)_2$ g. per litre	Specific conductivity mhos $\times 10^3$
Saturated 1.50 (Bassett)	8.75
,, $\times \frac{4}{5}$ 1.20	6.85
,, $\times \frac{1}{2}$ 0.75	4.5
,, $\times \frac{1}{4}$ 0.375	2.3
,, $\times \frac{1}{8}$ 0.1875	1.11
,, $\times \frac{1}{16}$ 0.094	0.558
,, $\times \frac{1}{40}$ 0.038	0.127

Preparation of Cement Pieces.

Neat cement was used in nearly all cases and gauged with water in the ratio 2 : 1. The cement was allowed to set in cylindrical brass moulds of inside diameter 1.7 cm. and height 0.95 cm.; pats made in this way weighed about 3.3 to 3.4 g. and had surfaces of 9.6 to 9.9 sq. cm. Coarse powders were made from these pats by grinding in an agate mortar. In some cases the powder was graded by selection between two sieves (0.5—1.0 mm.). Shaking of pats was done by hand or in a slow mechanical shaker, of powder by passing a current of air free from carbon dioxide. Conductivities were determined in an enclosed cell, from which samples could be siphoned for titrations, e.m.f. determinations, etc., or in some cases by the potentiometric method already referred to.

The results of extracting these cylinders at 25 deg. and under the conditions described are also represented graphically as A, B, N, and G. A and B were single pats; the ratio, volume of water in c.c. to their surface in sq. cm., was 15 : 1, and they were gently stirred by bubbling air free from carbon dioxide. N and G refer respectively to 6 and 5 pats; the ratio, volume of water to surface of cement, was 1.7 : 1 and they were stirred, G by shaking with the hand and N mechanically.

The concentrations of lime in solutions A and B did not rise in a few days to more than one-sixth of that which is in equilibrium with coarse or crystalline lime. The concentrations around A and B determined over periods from 100 to 200 hours eventually equalled or even surpassed the value for coarse lime.

In the sixth line results are rendered more comparable by reduction to a unit volume (of 100 c.c.) and surface of 1 sq. cm., which when multiplied by 1,000 represent the amounts dissolved by one litre from 1 sq. dm. of cement.

One litre of water will extract from 1 sq. dm. of cement surface amounts of lime varying from 2.7 to 3.7 g. in periods of from one to six days. Second extractions of surfaces such as A and B yield only about half as much lime as the first, the sums of the two extractions being nearly equal in the two cases. If the ratio of volume of water to surface of cement is much lower, as in G and N, the concentrations of lime are higher but a much longer time is required to extract the same amount, e.g. 100 hours for 2.76 g. per litre (G) per sq. dm. as against 48 hours for 2.75 g. per litre (A). With successive extractions, amounts in the

different experiments will depend on the depletion of the surface; thus A.1 and A.2 yield 4.3 g. per litre per sq. dm. in two extractions and three days, whilst G.1 and G.2 yield 4.96 g. in two extractions and 16 days. It seems likely that 5 g. per litre per sq. dm. is the minimum loss from massive cement pieces before the rate of corrosion begins to diminish. This corresponds to nearly 3½ litres of saturated lime solution. The lime lost is evidently only a small percentage of the pieces by weight, but this percentage will go on increasing with the surface-volume ratio of the cement, as is shown by our later experiments with powders.

EXTRACTION OF MASSIVE PIECES

Index No.	A		B		G		N
Weight, g.	3.32		3.35		16.4		7.9
Surface, sq. cm. ..	9.61		9.81		49.5		47.6
Extraction	A.1	A.2	B.1	B.2	G.1	G.2	
Time, hrs.	48	26	24	26	100	290	100
Concn. $Ca(OH)_2$, g. per litre	0.265	0.15	0.243	0.103	1.37	1.09	1.41
Vol. of soln., c.c. ..	150	150	150	150	83	83	83
Wt. of $Ca(OH)_2$ removed, g	0.0397	0.0225	0.0365	0.0154	0.114	0.091	0.117
Wt. of $Ca(OH)_2$ per 100 c.c. per sq. cm. surface × 1,000 ..	2.75	1.56	2.5	1.04	2.76	2.2	2.96

Effect of Aggregate.

It might be expected that the addition of inert material would diminish the rate and amount of corrosion by decreasing the active surface. On the other hand the surface is rough as compared with that of the neat cement, which was smooth; sometimes indeed the part in contact with the mould had a glassy lustre. Five pats T were made exactly the same shape and measured surface as

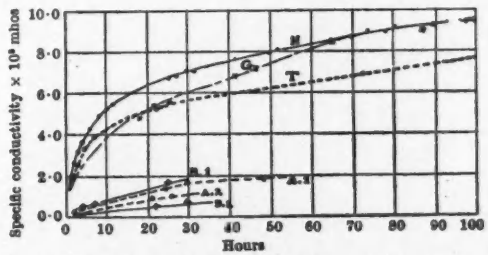

Fig. 2.—Concentrations of lime from cement pieces at various times.

G, but prepared from three parts of pure sand (washed and graded to 0.5—1.0 mm.) and one part of cement, gauged with water as usual, and set for a week in a moist atmosphere free from carbon dioxide. They were placed in 86 c.c. of conductivity water and the conductivity was determined at intervals:

Time in hours	1.0	3.0	7.0	24.12	70.0
Conductivity × 10^{-3} ..	1.54	2.65	4.08	5.52	6.8

The results are shown as a curve in *Fig.* 2. It will be observed that the first rate of attack is nearly the same as that of the neat cement N, but that after a few hours it decreases and after 70 hours there is distinct evidence that the corrosion is decidedly diminished.

Extraction of Powders with One Quantity of Water.

Limited volumes of water were kept with the ground set cement for several seeks at 25 deg. in absence of carbon dioxide and with occasional shaking. The solutions were analysed as before.

Sample I.—1.77 g. kept in 100 c.c. of pure water for 15 days. The hydrogen potential against a saturated potassium chloride-calomel electrode gave *p*H 12.3

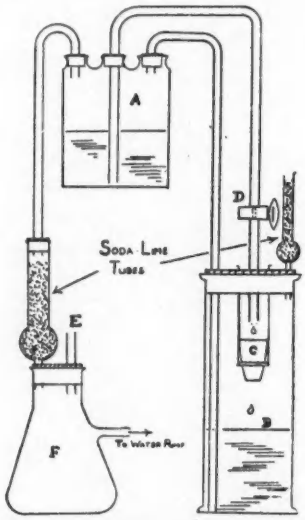

Fig. 3.—Apparatus for continued extraction of powdered cement.

(mean). A saturated solution of lime against the same half-cell gave *p*H 12.4—12.6. It is noticeable how little difference there is between the *p*H of saturated cement solutions and those of pure lime. Electrometric titrations showed a concentration of 1.36 g. of $Ca(OH)_2$ per litre, whilst that of pure lime gave 1.55 g. per litre. The amount of lime in solution corresponds to a loss of about 8 per cent. from the powder.

Sample K was kept in 200 c.c. of water free from carbon dioxide for one month *p*H 12.2 (mean.) Specific conductivity 6.96×10^{-3}, corresponding to 1.03 g. of $Ca(OH)_2$ per litre, but probably lowered by the presence of alumina.

Sample L.—3.47 g. kept in 100 c.c. of pure water for five weeks. *p*H 12.24. Specific conductivity 9.65×10^{-3}, corresponding to 1.42 g. of $Ca(OH)_2$ per litre.

Titration showed a concentration of lime which was higher than that of the saturated solution.

Extraction by "Soft" and "Hard" Waters.—Conditions were chosen so as to expose a large surface of cement for a long time to the same quantity of water in slow Movement. With this object a simple percolator (*Fig.* 3) was devised which worked very smoothly. The water was siphoned out of a reservoir (A) at a speed which was controlled by a tap (D), dropped into a Gooch crucible (C) containing powdered cement on a pad of cotton wool, and soaked through into a cylinder (B) from which it was drawn up from time to time into the upper reservoir by means of a suction pump attached to the flask (F). The volume of water was drawn ten times over about equal weights of cement. The soft water was the pure sample already described, whilst the hard water had the following characteristics (dissolved material expressed in parts per 100,000) : total solids 18.4 ; permanent (sulphate) hardness 8.1 ; temporary hardness 20.0 ; p_H (by hydrogen electrode) 8.0 ; specific conductivity 3.65×10^{-4} and 3.85×10^{-4} mho. Substances extracted were determined gravimetrically in the whole 300 c.c. and are expressed as amounts removed from the cement. Weights of cement were 3.163 g. (in soft) and 3.119 g. (in hard water).

	Pure Water		Hard Water	
	Wt. extracted	% on cement	Wt. extracted	% on cement
	g.		g.	
CaO	0.088	2.78	0.282	9.1
Fe_2O_3, Al_2O_3	0.002	0.06	0.005	0.16
So_3..	0.0034	0.11	−0.0086	−0.1

Thus more lime is dissolved by hard water than by the water free from carbonate. This somewhat unexpected result will be discussed when we have completed our experiments on carbonation. It is also worth noting that calcium sulphate was removed from a permanently hard water, which by filtering through powdered cement was changed from 8.1 to 5.2 degrees of hardness.

Extraction of Powder with Successive Quantities of Water.

In the following series, variation in the concentration of lime and in p_H was determined after each extraction. This may give some idea as to the variation of constituents in the surface layers, since p_H does not depend solely on concentration of lime but is also affected by dissolved aluminate and silicate.

A crushed sample was graded between 0.5 and 1.0 mm. diameter, so that 3.13 g. indexed as F had a calculated surface of 1,030 sq. cm. This was placed in 100 c.c. of pure water, saturated for various times by means of a current of hydrogen, the p_H being determined in the cell. The contents were then siphoned off, without contact with carbon dioxide, the conductivity determined by the method of potential fall, and in some cases the lime was titrated electrometrically.

These experiments were repeated with successive volumes of water for periods ranging from about 24 hours to several days, as shown in the appended table. After the twenty-fifth extraction quantities of 200 c.c. of water were used. The progressive fall both in lime content and in *p*H will be evident from *Fig.* 4 and from the selected values in the table.

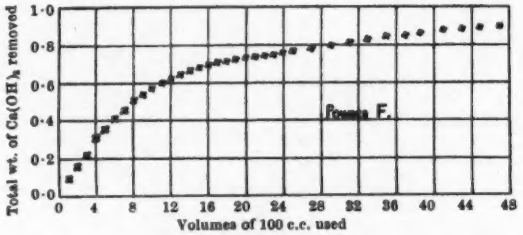

Fig. 4.—Extraction of powdered cement with successive quantities of water.

Index of extraction.	Sp. cond.	*p*H
1	7.5×10^{-3}	12.13
4	6.46 ,,	12.1
7	3.33 ,,	11.67
10	2.395 ,,	11.65
16	7.55×10^{-4}	10.9
24	7.65 ,,	11.1
34	2.96 ,,	10.75
36 (regrinding)	7.9 ,,	11.0

The residue, after extraction with a total of 4,800 c.c. of water, was ignited and analysed by the method already mentioned. The composition is compared with that of the original ignited cement and the amounts of each constituent extracted are obtained by difference.

	Original ignited, %	Extracted F, ignited, %	Extract from F, %
Insol. residue	0.315	2.2	—
SiO_2	22.25	20.8	1.35
Al_2O_3	6.85	6.7	0.15
Fe_2O_3	3.56	2.19	1.37
CaO	63.1	43.2	19.9
MgO	1.15	0.88	0.27
SO_3	0.92	—	0.92
		75.97	23.32

At the end of the later extractions *p*H had fallen to 10.7 or less, i.e. a lower value than corresponds with the final *p*H of the hydrolysable compounds. That this solution was not, however, yet in equilibrium, at any rate with the centre of the larger grains, was shown by a further experiment. The remaining powder was

reground and extracted with more water, when the pH rose to 11.0, κ to 7.9×10^{-4} (see table), therefore concentration of $Ca(OH)_2$ to 0.115 per litre. This experiment illustrates the extreme slowness of diffusion of lime through thicknesses of less than 05 mm. In fact it is only this slowness of diffusion which saves all cement from extensive disintegration by water. It is noted again that all the calcium sulphate has been removed, probably in the earlier stages of extraction.

COMPARISON OF EXTRACTIONS FROM PATS AND POWDERS IN 24 HOURS.

Index Letter.	N (pats)	O (powder)	F (powder)
Weight, g.	7.9	0.325	3.13
Surface, sq. cm.	7.6	12.9	1030
Vol. of water, c.c.	83	95	100
Ratio vol. to surface	1.74	7.36	0.097
$Ca(OH)_2$ g. per litre	0.952	0.95	1.1
Wt. $Ca(OH)_2$ in vol. used	0.079	0.09	0.11
Wt. dissolved per sq. cm. surface.. ..	0.00166	0.007	0.000107
Wt. per litre of solution and per sq. dm. surface	2.00	7.3	0.1065
Wt. of lime as per cent. by wt. of cement	1.0	27.7	3.5

It appears from these results that the most important single factor in determining specific amounts dissolved (last line) is the ratio of volume to surface, and that this ratio (fourth line) tends to be numerically equal to the ratio, wt. per

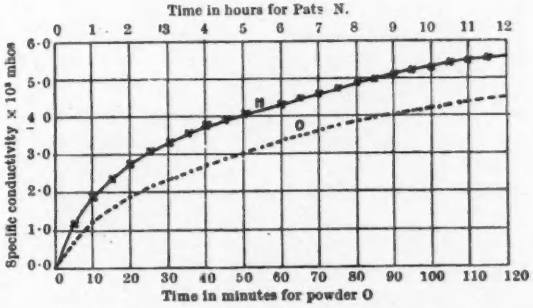

Fig. 5.—Velocity of corrosion of cement as pieces and powder.

litre per sq. dm. (eighth line) at any rate for a first extraction, with volumes of water which can reach a concentration of about 1 g. per litre of lime in 24 hours.

Velocity of Corrosion.

The methods are well adapted to show velocity of corrosion under various conditions, since by continuous stirring smooth curves are obtained as *Fig.* 5 for pats N. These curves might be expected to approximate to those expressing the dissolution of a soluble salt, etc., and to follow a unimolecular law provided that lime is supplied from the lower layers at a rate faster than that at which it diffuses through the concentration gradient in the solution. If log C is plotted

against t for pats N, a nearly linear graph is obtained from $t = \frac{1}{2}$ to $1\frac{1}{2}$ hours; the curve then bends over, again becomes linear from $t = 4$ to $t = 8$, and again with a lower velocity from $t = 8$ to $t = 11\frac{1}{2}$ hours. If C_s is the concentration of saturated lime solution with which it is supposed that the surface is in equilibrium, and if C_1, C_2 are the concentrations after times t_1, t_2, then a constant can be calculated from the results:

$$K = [1/(t_2 - t_1)] \log [(C_s - C_1)/(C_s - C_2)] \quad .. \quad .. \quad .. \quad .. \quad (1)$$

Taking intervals 2—7, 3—8, etc., a value of K can be calculated which varies from 0.0134 at $t_2 = 7$, $t_1 = 2$ to 0.0087 at $t_2 = 11.5$, $t_1 = 7$. All these values from $t_1 = 4$ to $t_2 = 11.5$ only vary between 0.0105 and 0.0087. Probably only for a short time at the beginning is the ordinary rate of dissolution of a soluble substance followed; after that it is determined by the rate of diffusion in the solid surface layers. The effect of depletion of surface layers is best shown in a powder, since supplies of highly concentrated lime from below should soon fail in this case.

The ground powder O was prepared for this purpose (from set cement one month old) and was selected by fractional sieving so that all particles had diameters between 0.5 and 1.0 mm. Of this powder 0.325 g. was placed in 95 c.c. of conductivity water at 25 deg. and readings were taken, at first every two minutes in an Arrhenius type of cell, of constant 0.101. The results are given below:

Time, minutes	Specific conductivity	Time, minutes	Specific conductivity
2	3.04×10^{-4} mho	60	3.36×10^{-3} mho
6	8.7 "	80	3.87 "
10	1.22 10^{-3} mho	100	4.21 "
20	1.88 "	140	4.72 "
30	2.26 "	200	5.02 "
40	2.71 "	120 hr.	7.6 "

The calculated surface was 12.9 sq. cm.

These results are shown for comparison with N on an extended time scale in *Fig.* 5. Over the range of 20 to 76 minutes a constant was found for equation (1) of a true solubility; although a slight drift was evident, e.g. from 0.0022 at the beginning to 0.0085 at the end of the interval, the mean value 0.00201 will express experimental results rather closely. Here the value of C_s is taken as that of saturated lime = 1.5 g. per litre. In the later stages, however, it must be supposed that the equilibrium concentration at the surface is no longer that of saturated lime. Thus after 120 hours the conductivity is 7.6×10^{-3}, which corresponds to a concentration of 1.1 g. of $Ca(OH)_2$ per litre, which will be nearly in equilibrium with the surface layers, the reaction having become very slow. Suitable lower values of C_s should give good constants at any stage. The lime in this extract was calculated from the conductivity and found to be 24.8 per cent. of the original powder. Quantitative experiments on the dehydration of set cement showed that it had combined with 27 per cent. of water and therefore there was 48.8 per cent. of lime in the set cement originally, whilst only 24.0 per cent. was present at the end. This powder will therefore have lost all its

mechanical strength by the time the conductivity of 83 c.c. of water has risen to 7.6×10^{-3}, the alkali reserves being sufficient even to saturate the water with lime.

Summary.

Conductivities and hydroxyl-ion concentrations (as *p*H by the hydrogen electrode) were used to determine the concentrations of calcium hydroxide dissolved from the pure solid as a standard. The solubility of pure lime obtained by these methods and potentiometric titration was found to be in good agreement with results of previous workers. The conductivity method, thus standardised, was found to be the more delicate in following slight changes of concentration.

These methods were then applied to an investigation of the corrosion of Portland cement by pure water, it having been found that the presence of aluminates and calcium sulphate dissolved from the cement had relatively slight effects.

Cylinders of neat cement were extracted with water under various conditions, and figures were obtained for the amounts of lime removed per unit surface of cement and volume of solution. For the same times, these amounts increase with increase in the ratios : surface of cement to volume of solution.

The initial effect of an inert aggregate on rate of corrosion was negligible, but in the later stages this rate was lower for a concrete than for a neat cement.

Rates of removal of lime and concentrations of extracts were compared in the cases of pats and powders respectively. About a quarter of the weight of powdered cement was removed by successive extractions with water. The most important factor governing the percentage dissolved is the ratio of volume of water to surface of cement.

The rate of corrosion of massive pieces in the early stages resembles the rate of dissolution of a pure substance, but in the later stages it appears to be more determined by rate of diffusion of lime through the surface of the solid.

A typical hard water was found to remove more lime than pure water under the same conditions, and the (sulphate) hardness of the water was thereby reduced.

Tensile Strength of Plain Concrete.—By A. Guttmann (*Zement*, 1935, p. 532.).—Concrete made with gravel aggregate of the usual sizes has a low tensile strength compared with its compressive strength when mixed somewhat wet in the usual manner. The ratio of tensile to compressive strength is usually less than that obtained in the standard tests. The tensile strength and also the ratio of tensile to compressive strength can be increased by using cement giving a concrete with a higher tensile strength, by the use of admixtures, by increasing the amount of mortar, by using a low water-cement-ratio, and by keeping the concrete wet during early hardening.

Notes from the Foreign Press.

Alum Size for Increasing the Impermeability of Concrete.—By W. Obst (*Zement*, p. 459, 1935).—It is well known that glue size makes concrete less pervious to water, but in time this may be washed out. If, however, 1 to 2 per cent. of alum is mixed with the cement and a 3 per cent. glue size is used only traces of glue can be discerned in the water which comes through a pat in the porosity test. This does not cause an increase in the setting time, and a higher compressive strength is obtained. The alum makes the glue insoluble, and a mixture of the two has been patented for making lime base colours impervious. Alum size also prevents efflorescence due to this property.

Optical Properties of α- and β-Dicalcium Silicate.—By N. Sundius (*Z. anorg. und allgem. chem.*, Vol. 213, pp. 343–352, 1933).—α-$2CaO.SiO_2$ in clinker usually forms rounded bodies with an imperfect prismatic cleavage parallel to the τ — direction (axis of elasticity Z) ; traces of cleavage also appear at right angles to this direction. The γ-direction is also the direction of the acute bisectrix (optical character positive). The crystals are always intricately twinned. The optical axial angle is 30 to 33 deg. and the birefringence 0.016 to 0.018.

β-$2CaO.SiO_2$ in clinker forms irregular sponge-like bodies. A strong cleavage is apparent which is approximately parallel to the γ-β-plane. In sections perpendicular to γ polysynthetic twinning can be seen which gives a pseudo-hexagonal appearance as the sections contain three parts each turned through 60 deg. with respect to the next. The optical axial angle is 73 deg. and the birefringence 0.021 to 0.023.

The α-form is usually brown or brownish-yellow. Inclusions in the β-form mark out the twinning lamellæ which occurred in the α-form before the inversion to the β-form. α-$2CaO.SiO_2$ is identical with the " belite " of Tornebohm, and β-$2CaO.SiO_2$ is " felite."

The β-$2CaO.SiO_2$ prepared by the author agrees in its properties with that prepared by Rankin and Wright, but this is not the case with α-$2CaO.SiO_2$.

The optical properties of synthetic α-$2CaO.SiO_2$ prepared by the author are : Twinning and general form as those found in clinker ; $2V = 36$ deg. ; $\alpha = 1.719$; $\gamma = 1.733$ (± 0.001) ; $\gamma - \alpha = 0.013 - 0.016$; it belongs to the triclinic system. The optical properties of β-$2CaO.SiO_2$ are : Twinning and general form as those in clinker ; sometimes pseudomorphous after the α-form ; $2V = 64$–69 deg. ; $\alpha = 1.717$; $\gamma = 1.736$ (± 0.001) ; $\gamma - \alpha = 0.020$–0.021 ; it probably belongs to the triclinic system.

The brown colour of α-$2CaO.SiO_2$ is due to the presence of minute inclusions of $4CaO.Al_2O_3.Fe_2O_3$, the amount of which can vary considerably. No $3CaO.Al_2O_3$ or $5CaO.3Al_2O_3$ was found to have been taken up in solution in α-$2CaO.SiO_2$ in any of the melts.

Clinker from shaft kilns often contains pure primary β-$2CaO.SiO_2$ but seldom pure α-$2CaO.SiO_2$ by itself ; usually there is a mixture of the two. In clinker from rotary kilns β-$2CaO.SiO_2$ is seldom observed and α-$2CaO.SiO_2$ is the chief orthosilicate ; therefore in this case the sintering of the clinker must have occurred above the α-β-inversion point. In the old shaft kilns the temperature must have been below 1,420 deg. C., but in rotary kilns it is undoubtedly above this. Cooling occurs so rapidly in the latter case that there is no time for inversion into the β-form.

Analysis of Set Concrete.

WE have received from Mr. W. St. B. More, the Honorary Secretary of the "Analysis of Set Concrete" panel of the Standards Association of Australia, a copy of the Australian Standard Method for the Analysis of Set Concrete. A method used in England was given in our issue for April, 1935, and a German method in our issue for November, 1935. The Australian method is as follows :—

(I) Explanatory and Scope.—The analysis of set concrete has for its main object the determination of the relative proportions of cement and aggregate in any sample. The determination of the "nominal mix" is often required, and a method for obtaining this is included. Certain cases of failure may be attributable to poor and badly proportioned aggregates, in which case a separation is essential ; in every case separation leads to useful information. The problem presents various difficulties. It may be that all the constituents of the concrete have similar compositions so that both physical and chemical methods of separation may become necessary. Basic slag aggregate, for instance, is almost impossible to separate chemically, whereas clean quartz aggregate makes the problem much easier. Limestone aggregates present obvious difficulties ; they are readily soluble in acid, and when impure simulate cement itself in composition.

The recommended methods which follow apply to normal concrete. Variations in procedure may be necessary in the treatment of, say, concrete containing aluminous cement, coke concrete, and concrete made from soft sandstone and some granites. It is therefore necessary that the solution of some problems be left to the analyst.

(II) Sampling.—The sample for analysis should be representative of the mass. No sample from a structure should weigh less than 10 lb. except in the case of mixtures containing very small aggregate. Accuracy of examination is increased if samples of the constituents used in making the concrete are available. In the event of samples of the cement used not being available or the brand known, the lime content may be assumed to be 62.5 per cent. and the soluble silica content 21.75 per cent. The assumption of a value, especially in the case of silica, is to be deprecated but may sometimes be unavoidable. If the "nominal mix" is required the sample should be of sufficient size to enable a representative sample to be taken for separation of coarse aggregate.

Where the nominal mix is not required, the whole of the sample submitted for analysis should be crushed to $\frac{1}{4}$ in. maximum size, and quartered carefully so that the final portion to be pulverised to pass an 80-mesh sieve will be truly representative.

Preliminary tests should be made to determine, if possible, the nature of the aggregate, e.g., action of hydrochloric acid, loss on ignition, etc. If the loss on ignition is found to be above 4.5 per cent. then it probably indicates the presence of limestone in the aggregate ; in this case it is necessary to determine the water of combination by, say, Penfield's method.

(III) Analysis.—Loss of Weight on Ignition.—Weigh 1 g. of the sample in a tared platinum crucible, and heat in a muffle furnace at 950 deg. C. for one hour.

Estimation of Acid Soluble Lime (to be done if the aggregates are free from soluble lime).—Weigh 2 g. of the prepared sample into a 400-cc. casserole and treat with 50 cc. of a 1 : 4 solution of hydrochloric acid. Place on a sand bath, cover with a clock glass, evaporate to dryness, and bake at a temperature not above 110 deg. C. for one hour. Take up with 75 cc. of 3N hydrochloric acid, warm, and filter through a 12.5 cm. rapid paper; wash with N hydrochloric acid several times, then with hot water, until free from chlorides. The lime in the filtrate may be estimated by any standard method.

Allowing for loss on ignition,

$$\text{Per cent. lime in loss-free sample } x = \frac{100 \times \%\text{ lime in sample.}}{100 - \%\text{ loss on ignition.}}$$

Therefore,

$$\text{total aggregate : cement} = \left(\frac{\%\text{ lime in cement}}{x} - 1\right) : 1$$

Example :—Per cent. lime in loss-free sample = 4.37 per cent., lime in cement = 61.33, therefore

$$\text{total aggregate : cement} = \left(\frac{61.33}{4.37} - 1\right) : 1 = 13 : 1$$

Estimation of Soluble Silica (to be done if the aggregates contain lime; the method may also be used as a check on lime estimation).—Weigh into a 400-cc. casserole 10 g. of the prepared sample. Moisten with a stream of hot water and agitate to produce a slurry. Break up any lumps with a glass rod. Add slowly 100 cc. of 3.3 N. hydrochloric acid (1 to 3 approximately), and stir thoroughly. Warm to complete reaction, allow the contents to settle, and decant through a 12.5-cm. fine filter paper into a porcelain basin. If it is necessary to use suction a flask of high alkaline resistance may be used; usually the filtration proceeds rapidly enough without any assistance. Retain as much of the residue in the casserole as possible. Wash twice by decantation with N. hydrochloric acid, then several times with warm water. Wash the precipitate off the paper back into the casserole. Add 75 cc. of freshly-prepared normal caustic soda solution, or normal carbonate of soda solution, to the residue in the casserole. Stir and heat to 75 deg. C. Decant as before through the same filter, and wash twice with weak caustic soda or carbonate of soda (about 60 cc.).

The filtrate now contains the silica in the form of silicic acid either in true solution or in suspension in the hydrochloric acid medium. Filter the first caustic soda filtrate into the acid filtrate, and start the evaporation of this at once. Catch the washings in a separate porcelain basin and add it to the main filtrate. Evaporate the solution to dryness on a water bath or on a hot plate, add 75 cc. of 2N to 3N hydrochloric acid, and heat to aid solution but do not boil. Filter through a 12.5 cm. rapid ashless paper and wash slightly. Again evaporate the filtrate to dryness, take up with acid and water, and filter through the same paper as before. If another paper be used, wash both with diluted hydrochloric acid

and finally with hot water until the washings are free from chlorides. Ignite the constant weight (*a*) in a platinum crucible, moisten the residue with water, add a few drops of concentrated sulphuric acid and approximately 5 cc. of hydrofluoric acid. Evaporate to dryness, ignite cautiously at first and finally to a bright red heat, cool and weigh (*b*).

The loss in weight $(a-b) \times 10$ = the percentage of soluble silica (deduct the percentage soluble silica found by experiment to be present in the aggregates, or 0.2 per cent. if samples of the aggregates are not available). Allow for water of combination (or loss on ignition if the method is used as a check on lime estimation).

Percentage of soluble silica in water, free sample

$$\times = \frac{100 \times \%\text{ soluble silica in sample.}}{100 - \%\text{ water of combination}}$$

Therefore total aggregate : cement $= \left(\frac{\%\text{ soluble silica in cement}}{x} - 1\right) : 1$

Example :—Per cent. silica in water, free sample = 2.68 ; per cent. soluble silica in cement = 21.30 ; therefore

Total aggregate : cement $= \left(\frac{21.30}{2.68} - 1\right) : 1 = 7 : 1$

If a sample of the original cement can be obtained, the soluble silica may be determined by the usual method or by the method described using $\frac{1}{2}$ g. sample. Owing to the small amounts of soluble silica usually yielded by the aggregates, the calculated cement content may be appreciably higher than that of the original concrete. With mixtures up to 7 : 1 this error is not of a serious nature, but increases progressively as the mix becomes weaker. If it is possible to obtain samples of the aggregates used a soluble silica determination will enable the analyst to make the necessary adjustment. In the absence of these samples a deduction of 0.2 per cent. is a satisfactory average figure.

Estimation of "Nominal Mix."—*Disintegration of Sample.*—Break a representative sample of the concrete (roughly 1,000 g.) with a hammer into lumps of 2-in. maximum size. If a compression machine is available it should be used in preference to a hammer. Heat the whole of the sample in a muffle furnace for three hours in a suitable container (a steel tray or box is satisfactory) to as high a temperature as the type of aggregate will permit (850 deg. C. is recommended for siliceous aggregates and 560 deg. C. for limestone). Cool and weigh the sample. The weight obtained at this point is taken as the combined weight of the original materials from which the concrete was made.

Separation of Coarse Aggregate.—Shake the sample gently in a closed tin for a minute or two to free the coarse aggregates. Screen through a 4-mesh sieve and then through an 8-mesh sieve. Pick out by hand the pieces between 4-mesh and 8-mesh, selecting the pieces that are obviously coarse aggregate, and adding them to the material retained on the 4-mesh sieve. Any mortar adhering to the stones after the shaking process may be scraped off with a knife. Weigh the coarse aggregate so obtained and estimate the percentage. Knowing the percentage of coarse aggregate and cement, the percentage of fine aggregate can be

obtained by difference and the " nominal mix " calculated as follows: Per cent. of coarse aggregate = Z, per cent. of fine aggregate = Y, per cent. of cement aggregate = X; nominal mix = $\frac{Z}{X} : \frac{Y}{X} : 1$.

Example :—Per cent. coarse aggregate = 50, per cent. fine aggregate = 40, per cent. cement aggregate = 10; nominal mix = $\frac{50}{10} : \frac{40}{10} : 1$, or 5 : 4 : 1

The recovery of coarse aggregate from concrete may be fairly complete, but the percentage obtained is not strictly accurate due to splintering during the heating process. It is not advisable to carry out analytical work on the sand-cement portion.

Practically all concrete in Australia is proportioned by volume. The fact that fine dry sand may bulk as much as 40 per cent. with the addition of 6 per cent. of water tends to show that this method of proportioning is not altogether satisfactory. Speaking generally, proportioning by weight sets a richer mixture than proportioning by volume for the same materials. The methods described refer to proportions by weight.

Possibility of Adulteration of Cement with Lime.—When the aggregates are siliceous the presence of hydrated lime may be indicated by determining the lime-soluble silica ratio in the concrete. If the ratio is higher than that obtained from the cement then it is probable that lime has replaced some of the cement.

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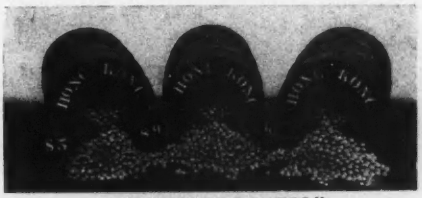

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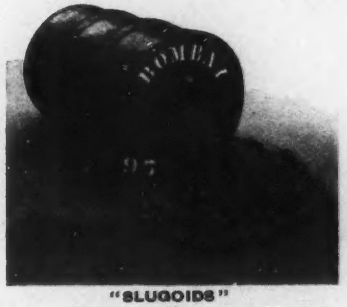

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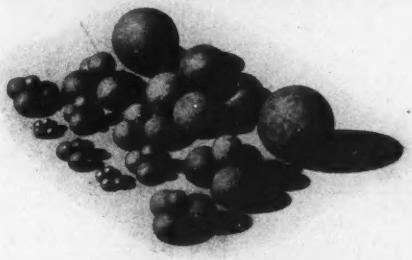

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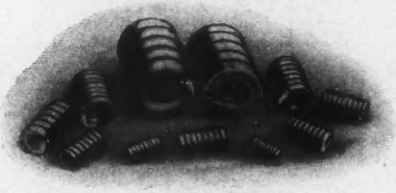

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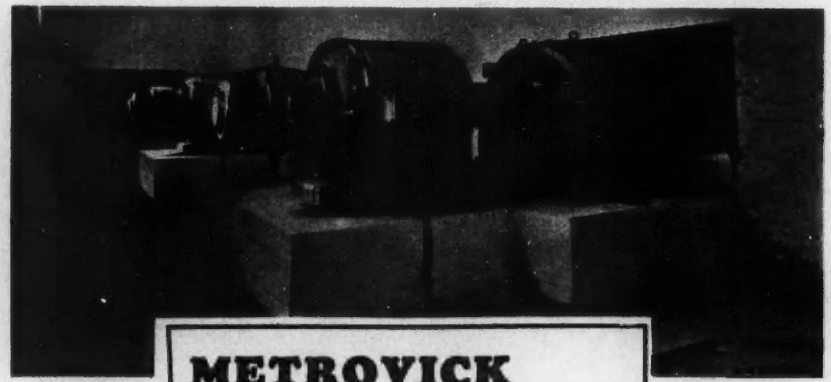

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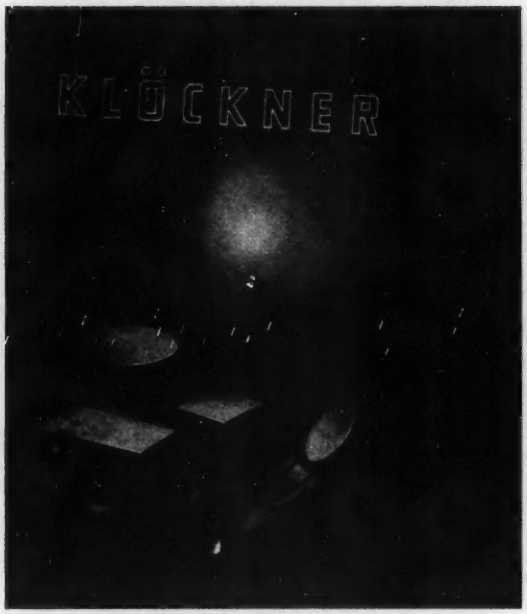

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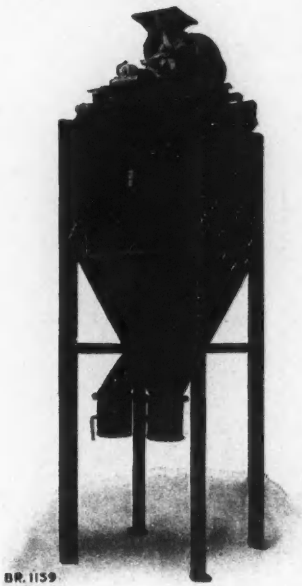

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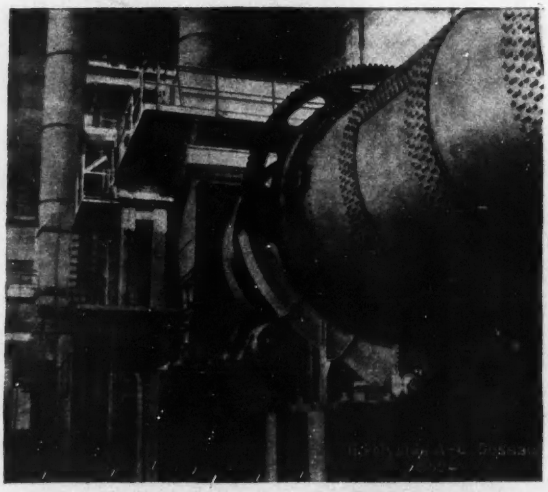

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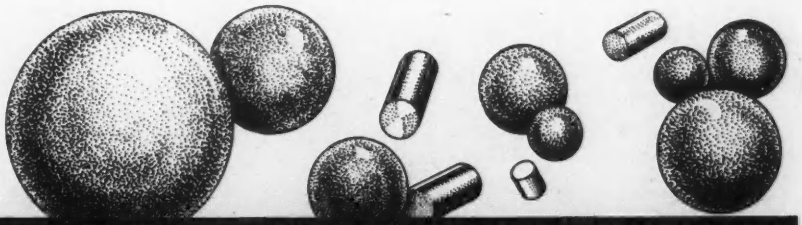

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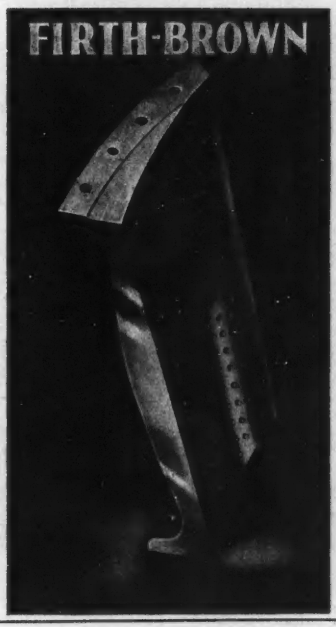

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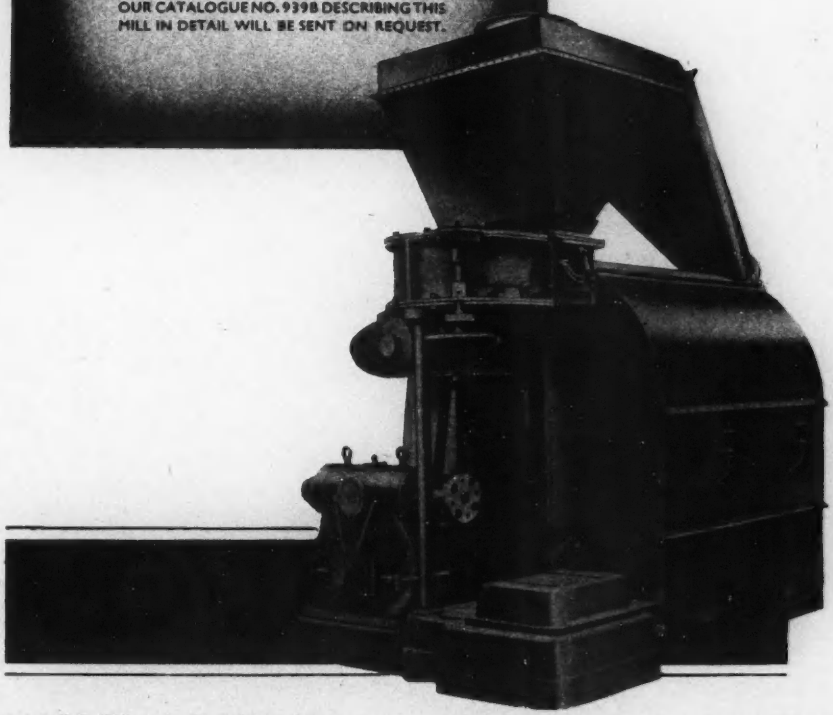

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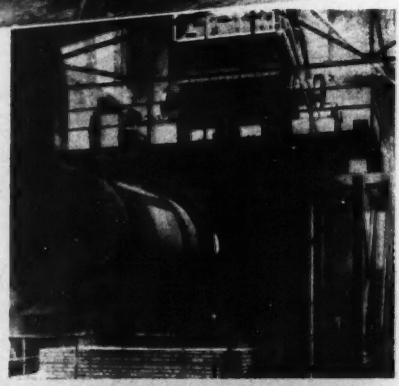

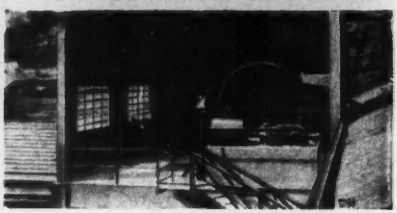

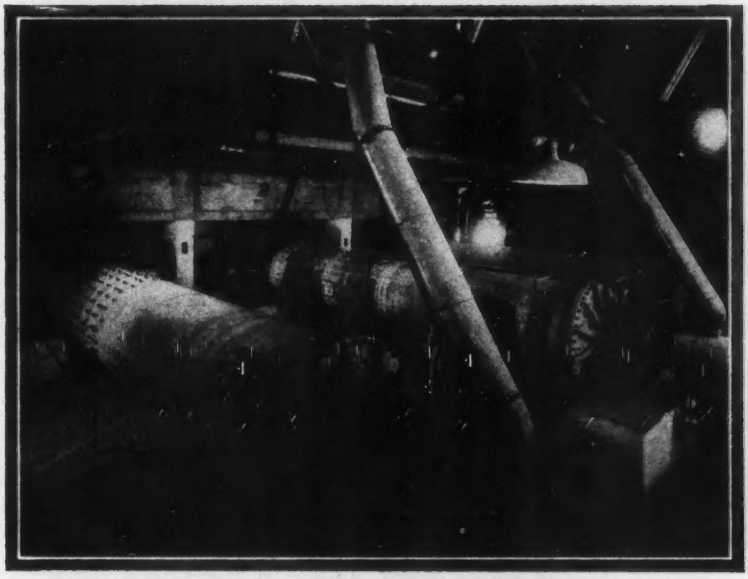

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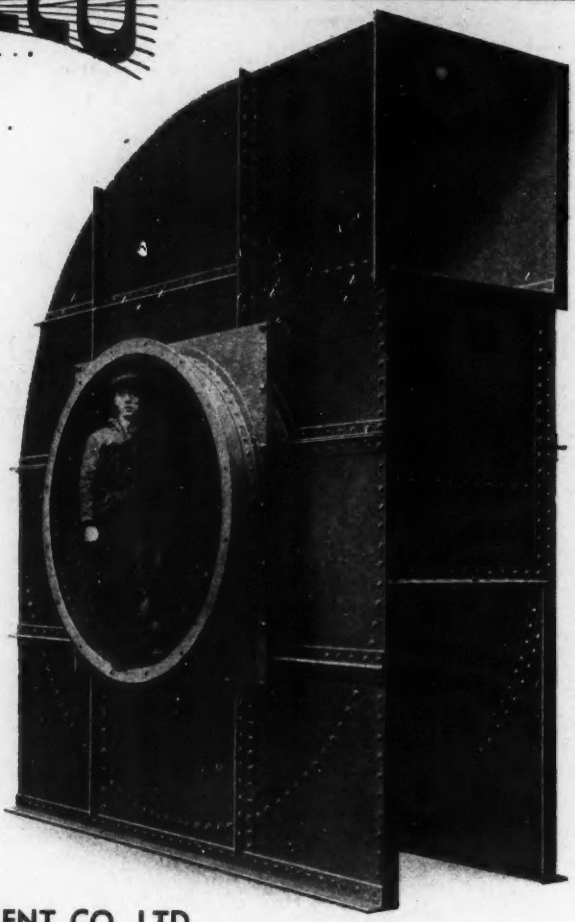

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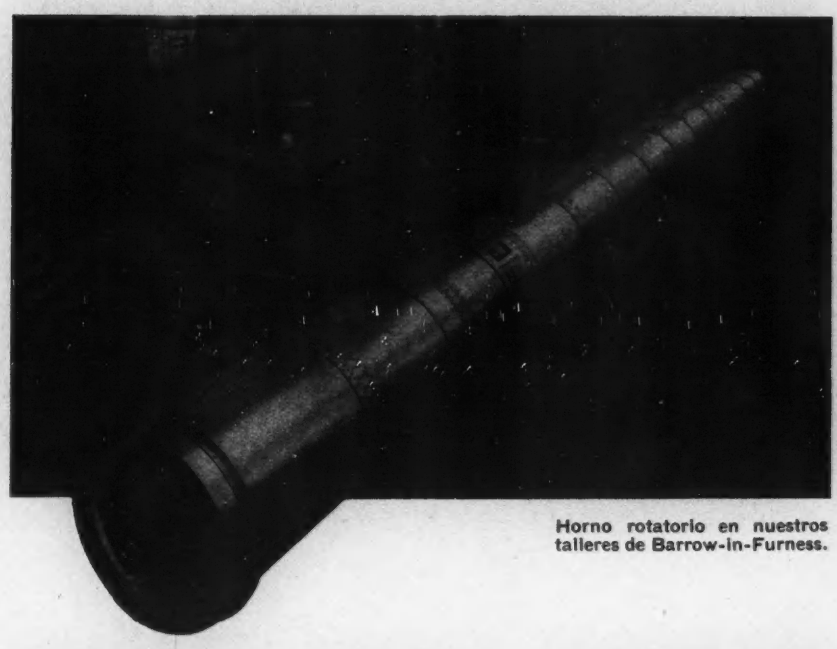

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